Chemistry 210
Exam II

University of Missouri-Columbia
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October 26, 1992

Name:

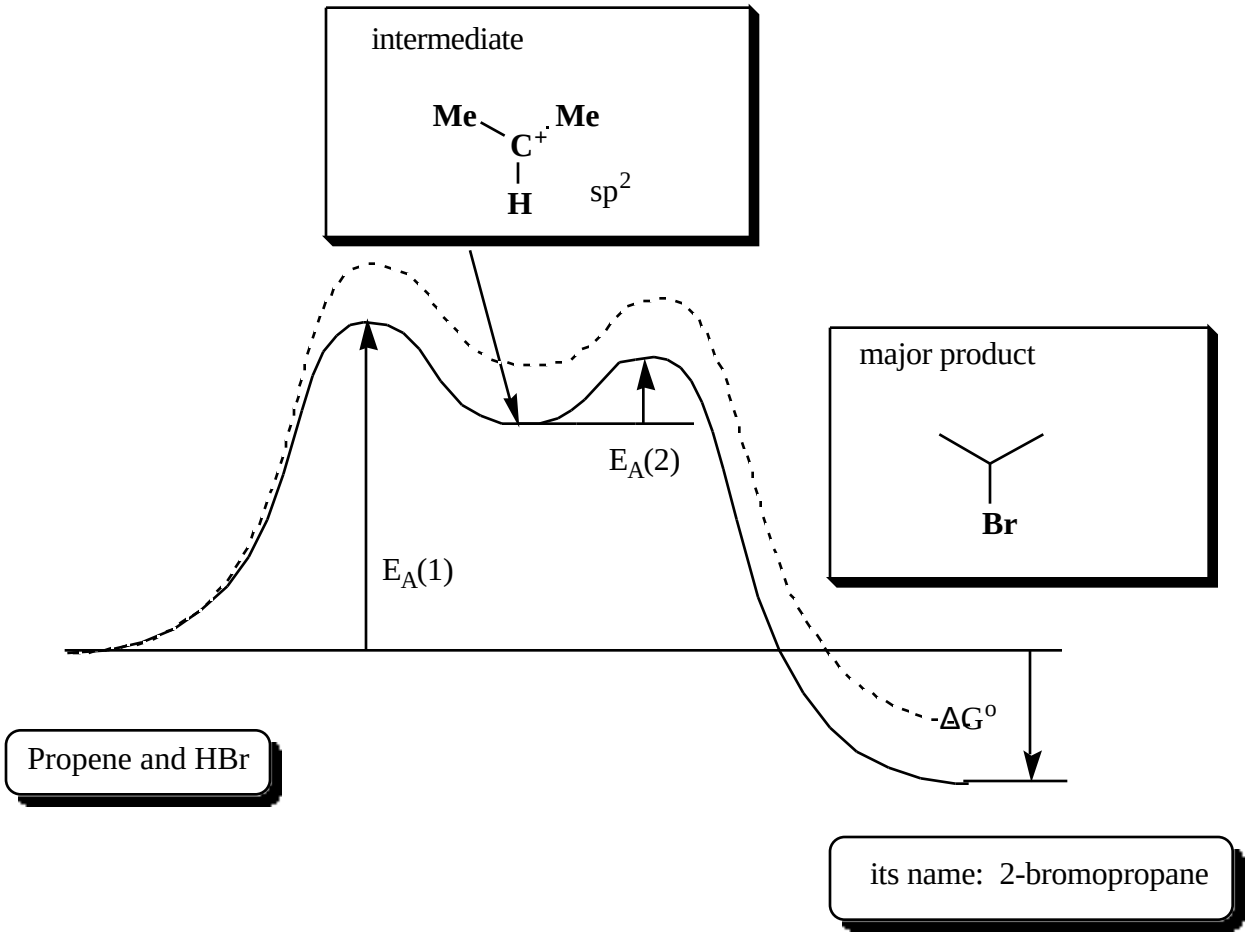
Answer Key

	Max.	Yours
Question 1	20	
Question 2	30	
Question 3	16	
Question 4	18	
Question 5	16	
Total	100	

Do not turn the page until advised to do so.

Question 1. HBr Addition Reaction and Potential Energy Diagram. (20 points)

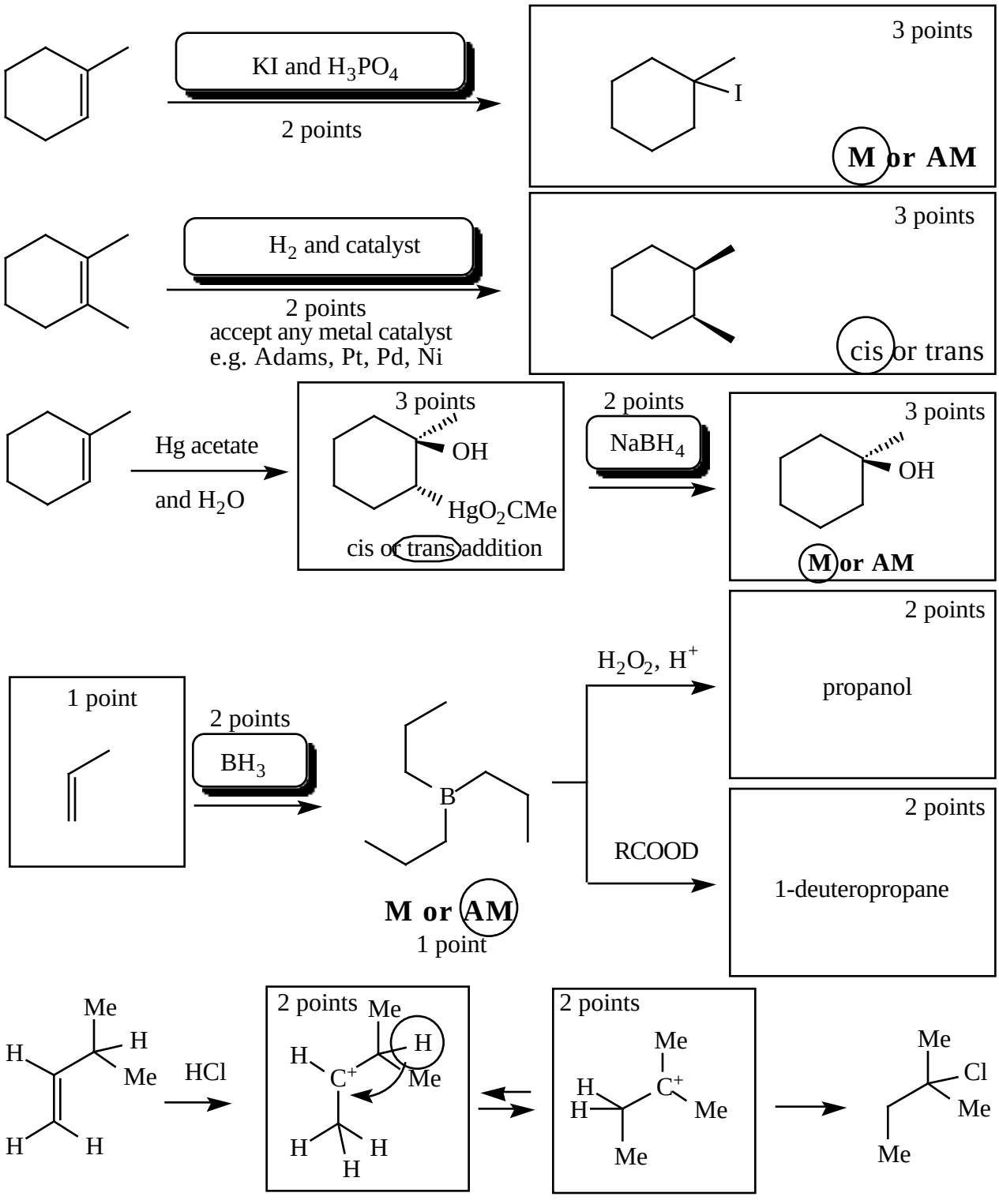
(a) The potential energy diagram for HBr addition to propene is shown schematically. This addition gives primarily the __Markownikow__ product because the formation of the __2˚__ (1˚, 2˚, 3˚) carbenium ion is favored over the formation ____1˚___ (1˚, 2˚, 3˚) carbenium ion in the first step. Draw the major addition product and give its name in the appropriate boxes. Draw the intermediate in the appropriate box and indicate the hybridization of the electron-deficient carbon.
(14 points total: 2-2-2 for the filling the spaces, 3 points for the major product and 1 points for its name, 3 points for the intermediate and 1 for its hybridization.)



(b) The primary bromide is formed only as a side product. Using Hammond's postulate, in the above diagram draw the appropriate curve for the side reaction schematically. (Hint: Think about whether the transitions states would be higher/lower for the side reaction.) (6 points).

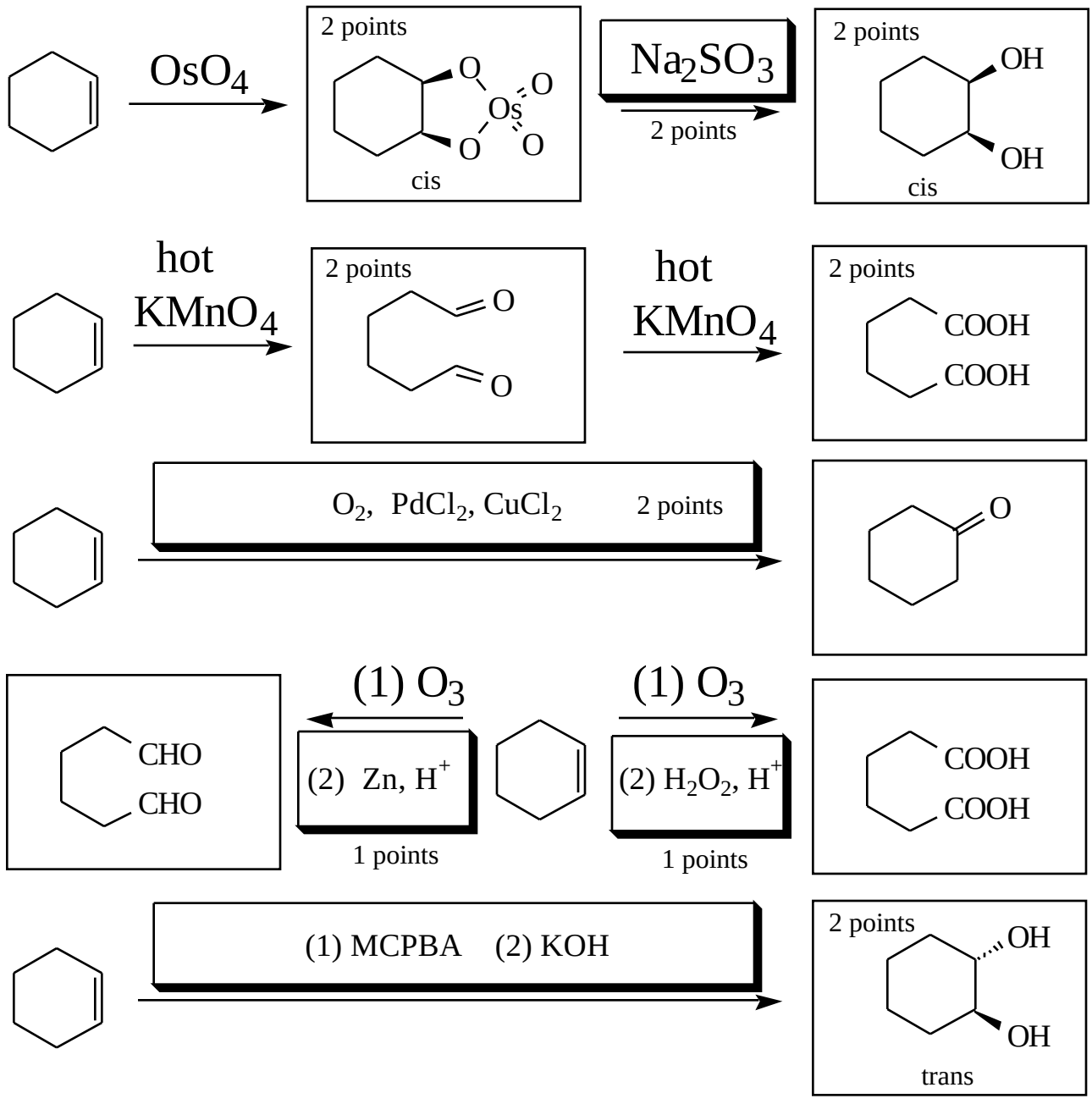
Question 2. Addition to Alkenes. (30 points)

Draw structures of products and intermediates. Give reagents were missing. Where indicated, circle M or AM and cis or trans as appropriate (M and AM indicate Markow. and Anti-M product formation, resp.).



Question 3. Oxidations of Alkenes. (16 points)

Let's look at oxidations of cyclohexene with different reagents. In each case, complete the reactions by specifying the reagents, by drawing structural formulas of the products, and -- in some cases -- by drawing the structural formulas of the intermediates. Specify whether cis or trans products if appropriate.



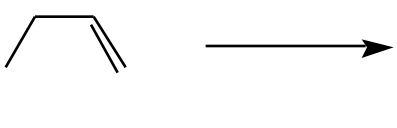
Question 4. Carbenes. (18 points)

(a) Briefly describe the Simmons-Smith method for the preparation of carbenes. (3 points)

CH_2I_2 and Zn(Cu) ---> I-CH_2-Zn-I

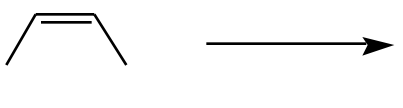
(b) For each of the four alkenes, give the structural formula of the starting material and of the product formed by reaction with CH_2. If there are several products, then give the structures of all. For the first three reactions, give the full names of the products including stereochemical descriptors as necessary.

1-butene (2 points for structures and 1 points for product name)



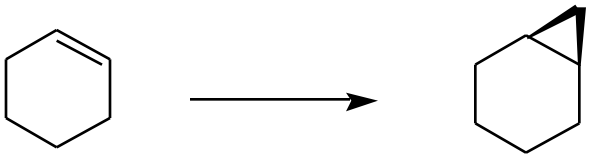
ethylcyclopropane

Z-2 butene (2 points for structures and 2 points for product name)



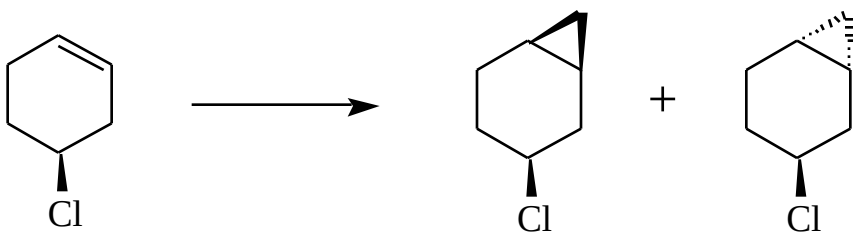
cis 1,2-dimethyl-cyclopropane

Cyclohexene (2 points for structures and 2 points for product name)



[4,1,0]-bicycloheptane

4-chlorocyclohexene (2 points for each product)

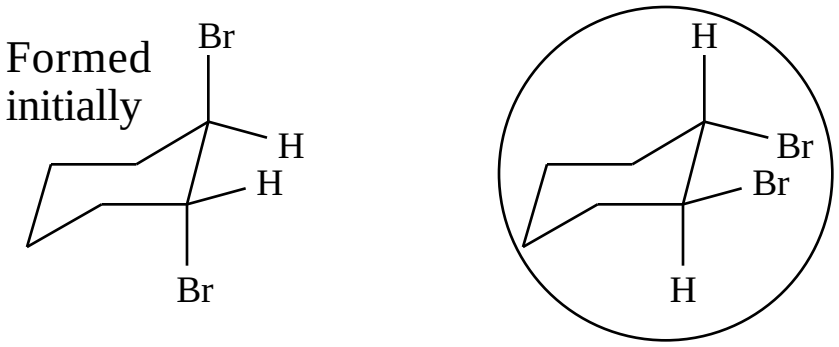


Question 5. Conformational Theory (20 points)

(a) For 1,2-disubstituted cyclohexanes two substituents S1 and S2 can be either "axial" or "equatorial" and there are the four possibilities shown. Mark which ones are "cis" or "trans". Examine the same question also for the 1,3-disubstituted system. (4 points, 0.5 points each field)

1,2-Disubst.			1,3-Disubst.		
S1	S2	Cis or Trans	S1	S2	Cis or Trans
axial	axial	***trans***	axial	axial	***cis***
axial	equatorial	***cis***	axial	equatorial	***trans***
equatorial	axial	***cis***	equatorial	axial	***trans***
equatorial	equatorial	***trans***	equatorial	equatorial	***cis***

(b) The bromination of cyclohexene involves the addition of two bromines from the ___opposite_____ (same, opposite) side(s) of the molecule because the mechanism involves a bridged __bromonium ion____ intermediate. Thus, the 1,2-dibromocyclohexane will have the *trans* ____configuration___ (conformation or configuration). The *trans* isomer gives rise to further isomerism because of possible ring-flips. The ring-flips convert _____conformational___ (structural, geometrical, conformational) isomers into each other. Draw perspective drawings of the two chair isomers of *trans*-1,2-cyclohexane. Circle the more stable isomer. Mark that isomer that would be formed if the ring-flips would not be possible (that is the primary product of the bromination). (16 points total: 2 points for each filled space, 2 for each correct drawing, 2 points for circle, 2 points for primary product).



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